Communication

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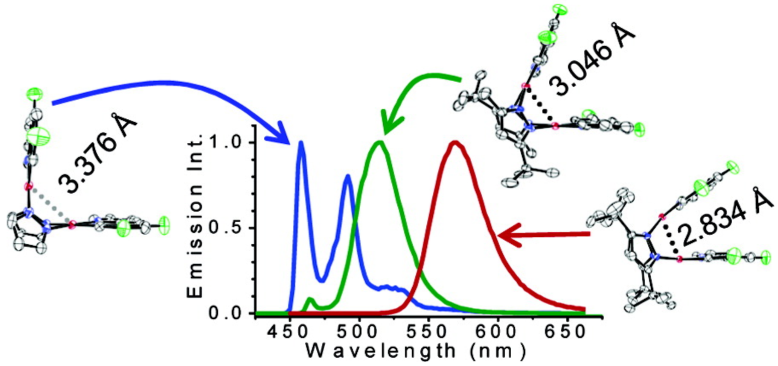

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Synthetic Control of Pt···Pt Separation and Photophysics of Binuclear Platinum Complexes

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Luminescent square-planar platinum(II) complexes have attracted a great deal of interest because of their potential applications in many fields, such as chemosensors,[1] photocatalysts,[2] light emitting diodes (LEDs),[3] and photovoltaic devices.[4] Emission from an isolated platinum(II) complex is typically assigned to ligand centered (LC) and/or metal-to-ligand charge transfer (MLCT) states. In addition, the square-planar Pt complexes have a rich excimer and aggregate/dimer photophysics,[5] leading to marked red shifts relative to the mononuclear emission spectra. These transitions are denoted as either metal−metal-to-ligand charge transfer (MMLCT) or excimeric ligand-to-ligand charge transfer. The MMLCT transition involves charge transfer between a filled Pt−Pt antibonding orbital and a vacant, ligand-based π^* orbital ($\sigma^* \rightarrow \pi^*$; see Figure 1 inset), often luminescing in the visible part of the spectrum.[6] The energy of the σ^* orbital, and thus the MMLCT excited state, shows a strong dependence on the metal−metal distance; the transition energy decreases with decreasing Pt−Pt separation.

In this communication, we report a series of pyrazolate-bridged cyclometalated platinum(II) complexes that have a boatlike conformation (Figure 2).[7] The bridging pyrazolate controls the degree of metal−metal interaction and, thus, the nature of the excited state. The complexes have the general formula $C^\wedge N\mathrm{Pt}(\mu\text{-}pz')_2\mathrm{Pt}C^\wedge N$ (where $C^\wedge N$ = 2-(2,4-difluorophenyl)pyridyl, pz' = μ-pyrazolate (**1**), 3,5-dimethylpyrazolate (**2**), 3-methyl-5-*tert*-butylpyrazolate (**3**), and 3,5-bis(*tert*-butyl)pyrazolate (**4**)) (see Supporting Information for syntheses). We have also prepared $C^\wedge N\mathrm{Pt(pz)_2BEt_2}$, **5**, which has an isolated Pt center (Figure 2).

The single-crystal X-ray structure of each complex has been determined. Complexes **1**−**4** have similar geometries, consisting of two square-planar Pt moieties, bridged by two μ-pyrazolate ligands in an exo-bidentate fashion (Figure 2).[7] The two $C^\wedge N$ ligands are oriented in a C_s symmetric manner for compounds **1**, **2**, and **4** (i.e., pyridyl group at the bottom in Figure 2a), while the $C^\wedge N$ ligands have a C_2 symmetric, opposed orientation in **3** (Figure 2c). The structural difference for **3** is most likely due to the asymmetric substitution of the pyrazolate, which leads to a steric preference for the opposed $C^\wedge N$ orientation. Substituting bulky groups to the 3- and 5-positions of the pyrazolate bridges forces the two $C^\wedge N$ Pt moieties closer together, decreasing the Pt−Pt distance. The Pt−Pt spacings are **1** = 3.3763(7) Å, **2** = 3.1914(9) Å, **3** = 3.0457(7) Å, and **4** = 2.8343(6) Å. A related μ-pyrazolate bridged binuclear Pt complex with thienylpyridine cyclometallating ligands ($C^\wedge N$) has a Pt−Pt spacing of 3.4863(6) Å,[7a] slightly longer than that observed for **1**. Despite the short Pt−Pt distance in **4**, the separation between the $C^\wedge N$ ligands ranges from 3.2 Å near the Pt atom to more than 5.1 Å at the periphery of the $C^\wedge N$ ligand; these values are outside of the distances expected for any $\pi-\pi$ interaction. Thus, we expect the principal effect of the increased steric bulk of the μ-pyrazolate in **2**−**4** is to enhance Pt−Pt interaction (stabilizing the Pt−Pt σ and destabilizing the σ^* bonding orbitals).[8] A number of platinum complexes exhibiting a range of Pt−Pt distances (and thus different photophysical properties) have been reported;[5,6] however, simple synthetic control of Pt−Pt separation, as illustrated here, has not been previously achieved.

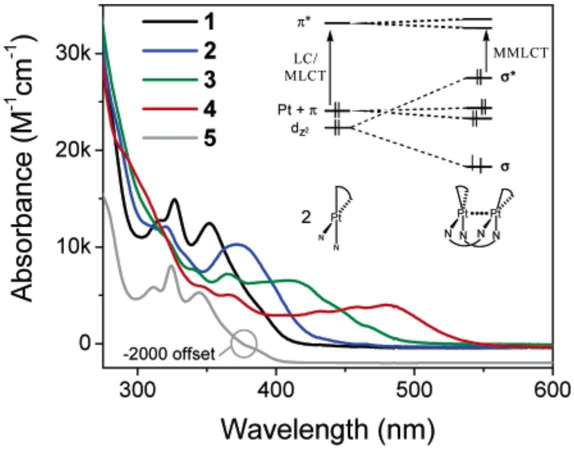

Figure 1. Absorption spectra for **1**−**5** (CH_2Cl_2 solvent, 298 K) are shown. Qualitative MO schemes for **1**−**4** and a mononuclear analogue are shown in the inset.

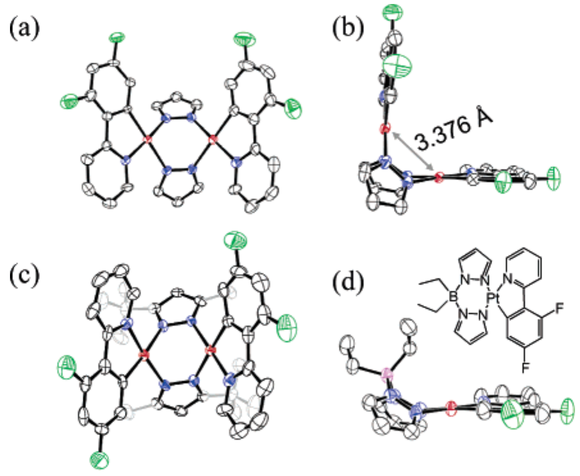

Figure 2. ORTEP views of **1**: (a) and (b), **3**: (c) and **5**: (d).

The complexes range in color, from yellow for **1** and **2**, to orange for **3**, and red for **4**. The UV−visible absorption spectra of **1**−**4** (Figure 1) show bands between 300 and 400 nm that are very similar to analogous bands in the related mononuclear species **5**; these are assigned to MLCT transitions.[9] Compound **5** has an extinction coefficient roughly half that of **1**, consistent with the lower molecular weight for **5**. For complexes **3** and **4**, a lower energy band is also observed between 400 and 550 nm ($\epsilon \approx 6000$ M^{-1}cm^{-1}); these bands are assigned to MMLCT transitions. The broad absorption bands red-shift with decreasing Pt−Pt distance,

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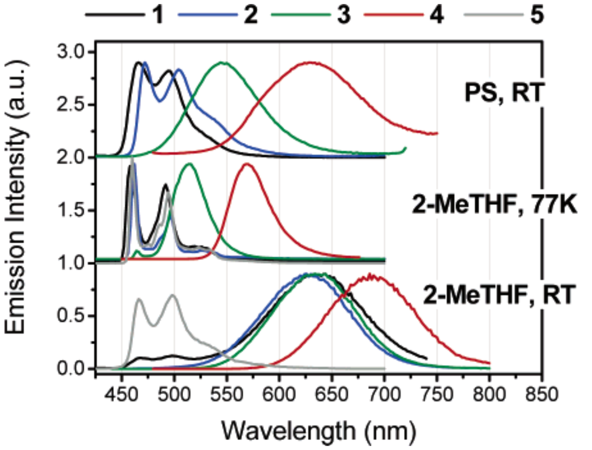

Figure 3. Normalized emission spectra of complexes **1**−**5** in 2-MeTHF solution (bottom and middle) and complexes **1**−**4** dispersed in polystyrene at room temperature (top).

indicating that the ^{1}MMLCT is strongly dependent on the Pt−Pt separation.

All four complexes emit in fluid solution, in the solid state (dispersed in polystyrene (PS)), and in 2-MeTHF glass at 77 K (Figure 3). Single-crystal emission spectra closely resemble the same spectra in PS (see Supporting Information). There is a large variation in the emission λ_{max} as a function of Pt−Pt distance for **1**−**4** in both glassy 2-MeTHF solution and dispersed in PS. The luminescent lifetimes (τ) for **1**−**4** are in the microsecond regime, indicating that the emission is phosphorescence. For example, $\tau = 2.4\ \mu$s for **1** and $\tau = 1.4\ \mu$s for **4**, in PS at room temperature. The emission spectra for **1**−**4** in 2-MeTHF at 77 K narrow considerably, and the λ_{max} blue-shift to 458, 462, 515, and 570 nm, respectively. The emission line shapes of **1** and **2** at 77 K have distinct vibronic features, similar to the mononuclear analogue **5** and have $\tau = 8.5$ and 7.4 μs, respectively. In contrast, complexes **3** and **4** display broad, featureless emission spectra at 77 K, with $\tau = 4.1$ and 5.4 μs, respectively, consistent with an assignment to a triplet metal−metal-to-ligand charge transfer (^{3}MMLCT) transition. The photophysical properties of **1** and **2** in fluid solution differ from those in the solid state. Complexes **1** and **2** display broad featureless spectra similar to **3** in fluid solution. Complex **1** also shows additional emission features between 450 and 525 nm, consistent with mononuclear emission. In contrast, the mononuclear analogue, **5**, shows only blue structured emission in all solution media.

For complexes **1** and **2** in the solid state, the close similarity of the emission spectra to that of **5** indicates luminescence originating from a mixed ligand center triplet/metal-to-ligand charge transfer (^{3}LC/MLCT) excited state, consistent with little-to-no metal−metal ground-state interaction under these conditions. On the other hand, for complexes **3** and **4** in the same rigid media, only ^{3}MMLCT emission is observed, indicating that a strong intramolecular Pt−Pt ground-state interaction exists in both of these complexes. The complex with the shortest Pt−Pt spacing, **4**, displays red emission, while the complex with an intermediate Pt−Pt spacing, **3**, gives green emission. In fluid solution, all four binuclear complexes readily collapse into the ^{3}MMLCT excited state, giving a broad featureless, red emission. In the ^{3}MMLCT excited state, the σ* orbital is depopulated, which shortens the Pt−Pt bond. A similar bond shortening process has been experimentally observed for other d^8−d^8 Pt binuclear complexes.[10] The enhanced Pt−Pt interactions destabilize the σ* orbital and, in fluid solution, lead to luminescence that is red-shifted relative to emission from complexes with static, ground-state structures, as occurs in the PS and 77 K samples. Whereas all four complexes can relax into the ^{3}MMLCT excited state in fluid solution, the samples in PS (and at 77 K) retain their equilibrium ground-state structures and the two which have a σ* HOMO, **3** and **4**, continue to display MMLCT absorption and emission.

The color control and bright luminescence of **1**−**4** in the solid state make these complexes materials of interest for application as phosphorescent emitters in organic LEDs; these device results will be reported elsewhere. It has also not escaped our notice that the shortening of the Pt−Pt distance in the excited state of these binuclear Pt complexes makes them ideal candidates for photoactuated nanohinges and nanotweezers.

Acknowledgment. We thank the Universal Display Corporation for financial support of this work.

Supporting Information Available: X-ray crystallographic data in CIF format, synthetic procedures, characterization data, and photophysical data are given for **1**−**5** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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